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(54) PRODUCTION OF STRETCHED FILM OF POLYLACTIC ACID POLYMER

(57)Abstract:

PURPOSE: To produce a film having practical strength from a polylactic acid polymer having biodgradable properties.

CONSTITUTION: A non-stretched sheet of a polylactic acid polymer is longitudinally stretched at stretching temp. of 50-90°C within a stretching magnification of 1.5-5 times so that the degree (Ana of in-plane orientation becomes a range of 3.0×10-3-30×10-3 and subsequently laterally stretched at stretching temp. of 50-80°C within a stretching magnification range of 1.5-5 times to produce a sequential biaxially stretched film. After biaxial stretching, if the biaxially stretched film is heat-treated within a temp. range of 70°C-(m.p. of polymer), the thermal dimensional stability thereof is enhanced. By this constitution, the brittleness of the film is improved and stretching processing can be stably performed.

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CLAIMS

[Claim(s)]
[Claim 1] The polylactic acid system polymer which carries out vertical extension of the non-extended sheet of a polylactic acid system polymer within the limits of the extension temperature of 50-90 degrees C and 1.5 to 5 times as many draw magnification as this so that amount-of-preferred-orientation within field deltan may become within the limits of 3.0x10-3 to 30x10-3, and is subsequently characterized by carrying out horizontal extension within the limits of the extension temperature of 50-80 degrees C and 1.5 to 5 times as many draw magnification as this is the manufacture approach of a biaxial oriented film serially.
[Claim 2] The manufacture approach according to claim 1 characterized by heat-treating after biaxial extension at the temperature of 70 degrees C - (melting point of a polymer) within the limits.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] the manufacture approach of a biaxial oriented film that this invention consists of polylactic acid system polymers, such as Pori L-lactic acid, Pori D-lactic acids, or these copolymers, -- it is serially related with the manufacture approach of a biaxial oriented film in detail.
[0002]
[Description of the Prior Art] It excels in current and transparency and the polyethylene terephthalate oriented film etc. is known as a high ingredient of a mechanical strength. While dimensional stability can be given by heat-treating for that semicrystallinity, this film reduces degree of crystallinity by copolymerization, and is used also as a shrink film. The rate of being used for the package field as these applications is also high. However, if these ingredients are rejected under natural environment, they remained without understanding the part for the stability, spoiled the scene, and have caused the problem of polluting the living environment of a fish, a wild bird, etc.
[0003] Then, the film which consists of a resolvability polymer which does not produce these problems is demanded, and many researches and development are actually performed. There is polylactic acid as the example. Hydrolysis advances automatically in soil and, as for polylactic acid, it is known that the original form will all subsequently serve as a harmless decomposition product by the microorganism into soil.
[0004] However, it is weak, and the film of polylactic acid cannot bear practical use, but reforming of physical properties is required for it. Although extension processing is mentioned as one of the reforming approaches of film physical properties, about the extension approach of polylactic acid, and especially the serial biaxial extension approach useful as a industrial processing method, it is hardly known until now.
[0005] Serially, by the biaxial extension approach, since the method extended in a longitudinal direction is used after extending to the first step in a lengthwise direction in many cases, the reinforcement and the physical properties of the biaxial oriented film with which the physical properties immediately after extending to a lengthwise direction not only influence the ductility to the next longitudinal direction, but are finally manufactured are also influenced.
[0006]
[Problem(s) to be Solved by the Invention] This invention aims at offering extension [in / serially / biaxial extension] processing conditions useful as that extension approach and an especially industrial processing method, in order to obtain the polylactic acid system polymer film equipped with the practical reinforcement which can be used for example, for a package application.
[0007]
[Means for Solving the Problem] This invention is the manufacture approach of the serial

biaxial oriented film of the polylactic acid system polymer which carries out vertical extension of the non-extended sheet of a polylactic acid system polymer within the limits of the extension temperature of 50-90 degrees C, and 1.5 to 5 times as many draw magnification as this so that amount-of-preferred-orientation within field deltan may become within the limits of 3.0x10-3 to 30x10-3, and is subsequently characterized by carrying out horizontal extension within the limits of the extension temperature of 50-80 degrees C, and 1.5 to 5 times as many draw magnification as this. Furthermore, when giving heat dimensional stability, after carrying out biaxial extension, it is characterized by heat-treating by the temperature of 70 degrees C - (melting point of a polymer) within the limits.

[0008] Hereafter, this invention is explained in detail. The polylactic acid system polymers in this invention are the copolymers of polylactic acid or a lactic acid, and other hydroxycarboxylic acid, or such mixture, and other polymeric materials may be mixed within limits which do not check the effectiveness of this invention. Moreover, it is the purpose which adjusts fabrication nature and film physical properties, and it is also possible to add additives, such as a plasticizer, lubricant, an inorganic filler, and an ultraviolet ray absorbent.

[0009] As a lactic acid, L-lactic acid and D-lactic acid are mentioned and a glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyrate, a 3-hydroxy valeric acid, a 4-hydroxy valeric acid, a 6-hydroxy caproic acid, etc. are mentioned as other hydroxycarboxylic acid.

[0010] As these polymerization methods, a condensation-polymerization method, a ring-opening-polymerization method, etc. are possible also for adopting which a well-known approach, and may use still a small amount of chain elongation agent for molecular-weight increase, for example, a diisocyanate compound, a diepoxy compound, an acid anhydride, etc. as the weight average molecular weight of a polymer -- 10,000- if 1000 and 000 are desirable and less than this range, when it will hardly be discovered and practical use physical properties will exceed, melt viscosity becomes high too much and is inferior to fabrication nature.

[0011] The film production conditions of a non-extended sheet are explained. A polylactic acid system polymer is fully dried, and after removing moisture, it fuses with an extruder. Since melting temperature changes with presentations, choosing suitably corresponding to it is desirable. A 140-230-degree C temperature requirement is usually chosen in fact.

[0012] As for the polymer by which melting shaping was carried out at the shape of a sheet, it is desirable to make the rotating casting drum (cooling drum) contact, and to quench. 50 degrees C or less are suitable for the temperature of a casting drum. If higher than this, a polymer adheres to a casting drum and it cannot take over. Moreover, it is desirable for crystallization to be promoted, to set it as the above-mentioned temperature requirement, to quench, since it becomes impossible for a spherulite to progress and extend, and to make it parenchyma top amorphism nature.

[0013] Next, the extension approach is explained. In this invention, the film after vertical extension has the amount of preferred orientation within a field important for 3.0x10-3 to 30x10-3, and being 5.0x10-3 to 30x10-3 preferably (deltan). If lower than this, the tension tenacity and elongation to the lengthwise direction of the biaxial oriented film finally manufactured will be low, practical use will not be borne, but if higher than this, orientation crystallization will be promoted, and the problem of a film fracturing at the time of the next horizontal extension arises. Generally the range of extension temperature is 50-90 degrees C, from this, ductility is low at the time of low temperature, and a film tends to fracture it at the time of extension. Moreover, if higher than this, the inclination for the extension effectiveness to become small will be shown and it will be easy to produce extension nonuniformity. A 55-80-degree C temperature requirement is chosen more suitably.

[0014] Draw magnification is preferably chosen within the limits of two to 4 times 1.5 times to 5 times. If deltan becomes [draw magnification] smaller than the aforementioned value under in this range and draw magnification crosses this range, even if about [not being desirable] and

a vertical oriented film is obtained, it will be hard coming for the fracture under film manufacture to occur frequently, and to carry out horizontal extension next. Within the limits of the above, deltan obtains the vertical oriented film of 3.0x10-3 to 30x10-3 by choosing extension temperature and the combination conditions of draw magnification.
[0015] After carrying out vertical extension the above condition, it extends in a longitudinal direction. 50-80 degrees C of extension temperature of horizontal extension are preferably chosen within the limits of 55-70 degrees C. At the temperature of less than 50 degrees C, it can hardly extend. Moreover, since crystallization temperature is falling, at the temperature exceeding this range, crystallization is promoted during extension and a film becomes easy to fracture the film after vertical extension during manufacture. Draw magnification is chosen within the limits of 1.5 to 5 times. In under this range, the tension tenacity and elongation to the longitudinal direction of the biaxial oriented film which an orientation effect is not acquired but is finally manufactured does not occur frequently and have the desirable fracture under film manufacture, if practical use is not borne low and draw magnification crosses this range.
[0016] A well-known approach is sufficient as the extension approach, for example, vertical extension can be extended, heating between two rolls with a peripheral-speed difference, and using a tenter, grasping film both ends with a clip, horizontal extension can make train spacing of a clip train able to expand, and can be extended.
[0017] It heat-treats in 70 degrees C - (melting point of a polymer) a temperature requirement to give the dimensional stability (heat dimensional stability) under temperature a little higher than ordinary temperature to a film. Under in this range, crystallization is not fully promoted and heat setting is not fully carried out. That is, heat dimensional stability is low. On the other hand, Siwa, generating of nonuniformity, nebula-ization, etc. are caused to a film in the heat treatment temperature exceeding this range. Heat treatment time amount is good in about 3 - 60 seconds. As for heat treatment, it is advantageous practically to carry out by grasping film both ends with a clip within a tenter following on horizontal extension.
[0018] Although this invention is hereafter explained concretely from an example, the measuring method of the physical-properties value in this invention is as follows.
(1) The amount of preferred orientation within a field (deltan) : it measured and asked for the birefringence in a film with the polarization microscope.
deltan=R/dR: Retardation Film thickness [d:] (2) tension tenacity and elongation: Based on JIS-K -7127, it measured using the tensilon by Oriental energy machine company 2 mold machine. A lengthwise direction is written by MD and a longitudinal direction is written by TD.
(3) Contraction : in order to evaluate heat dimensional stability, the film sample was started to 100mmx100mm, after being immersed in the 80-degree C warm water bus for 10 seconds, the dimension in every direction was measured, and the percentage showed a contracted part to the original dimension. A lengthwise direction is written by MD and a longitudinal direction is written by TD.
[0019]
[Example]
(Example) The Pori L-lactic acid (melting point of 175 degrees C) of weight average molecular weight 100,000 [about] was cooled by casting drum lifting which held at melting extrusion and 32 degrees C at 180 degrees C, and the 200-micrometer non-extended sheet was obtained. After carrying out the preheating of this non-extended sheet with a metal roll, it extended to the lengthwise direction between rolls with a peripheral-speed difference, heating at an infrared heater. It continued, and horizontal extension was carried out by the tenter and the vertical oriented film was succeedingly heat-treated within the tenter. Extension conditions and heat treatment conditions were changed, and the film sample shown in Table 1 was obtained. The pass time of extension / heat treatment each zone in about 3m a part for /and a tenter of the flow rate of a film is 20 seconds, respectively. The property of the obtained film is shown in

Table 2.
[0020]
[Table 1]

表 1

No		1	2	3	4	5	6	7	8	9	10	11	12	13	14
縦延伸	温度（℃）	未延伸シート	60	45	95	60	60	80	75	60	60	60	60	60	60
	倍率（倍）		2.6	2.6	2.6	1.3	6.0	1.5	5.5	2.6	2.6	2.6	2.6	2.6	2.6
	安定性		○	×	×	○	×	○	○	○	○	○	○	○	○
	$\Delta n \times 10^{-3}$		5.8	—	—	2.1	—	2.3	33.1	5.8	5.8	5.8	5.8	5.8	5.8
横延伸	温度（℃）		60	—	—	60	—	60	60	60	60	60	60	60	60
	倍率（倍）		3.3	—	—	3.3	—	3.3	1.5	1.3	5.5	3.3	3.3	3.3	3.3
	熱処理温度（℃）		100	—	—	100	—	100	—	100	—	80	140	65	180
	安定性		○	—	—	○	—	○	×	○	×	○	○	○	○

[Table 2]

表 2

No			1	2	3	4	5	6	7	8	9	10	11	12	13	14
フィルム物性	引張強度（kgf／cm²）	MD	648	900	—	—	710	—	630	—	1030	—	950	910	940	—
		TD	641	1060			1350		1300		690		1110	1060	1090	
	伸び（%）	MD	4	92	—	—	3	—	4	—	92	—	88	95	91	—
		TD	4	87			81		83		3		81	90	81	
	収縮率（%）	MD	0	2	—	—	0	—	0	—	2	—	6	1	18	—
		TD	0	1			2		1		1		4	0	19	
総合評価			×	◎	×	×	△	×	△	×	△	×	○	◎	○	×

[0021] The passage clear from the result shown in Table 1 and Table 2, the stable vertical extension and horizontal extension are possible for No.2 vertical extension conditions and whose horizontal extension conditions are within the limits of this invention, and 11-13, and the obtained film has the outstanding strong ductility. No.3-8 with this invention out of range are inferior in vertical extension conditions in respect of the stability of extension, or film physical properties. Although vertical extension conditions are within the limits of this invention, they are inferior to extension stability or film physical properties also in No.9-10 with horizontal extension conditions out of range.

[0022] Moreover, although the film of No.13 of this invention is excellent in respect of extension stability and film reinforcement, contraction is high, and when obtaining a film with still higher heat dimensional stability, it is understood are good to heat-treat at the temperature of 70 degrees C or more like No.11-12. In addition, in No.14, since heat treatment temperature was too high, while Siwa and nonuniformity occurred on the film, the film milked partially, and a good biaxial oriented film was not obtained.
[0023]
[Effect of the Invention] According to this invention, serially, by adopting the extension conditions of the specific range in manufacture of the biaxial oriented film of the polylactic acid by the biaxial extending method, the brittleness of a film is improved, and it is stabilized and extension processing can be performed. Moreover, dimensional stability could be given by selecting suitable heat treatment conditions, without spoiling the workmanship of a film, especially an appearance. Since the film obtained has the so-called biodegradability, it can be conjointly used suitable for the package field etc. with the outstanding strength property.

[Translation done.]